

Attachment A

TH-0681 PCT, Report of additional experiments

2-Alkyl branched alcohols, having a total of 14, 15 and 16 carbon atoms respectively including their alkyl branches which were methyl, ethyl, propyl, butyl or hexyl, were purchased and used. All branched alcohols were characterised by ^{13}C NMR and found to be greater than 97 % pure. All alcohols were converted to alcohol sulphate sodium salts with ClSO_3H followed by neutralisation with NaOH , as described in Example 6 of the application.

The branched alcohol sulphates were subjected to detergency tests using the laboratory radiotracer detergency procedure of W.T. Shebs and B.E. Gordon, J. Am. Oil Chem. Soc., 45 (1968) 377 and J. Am. Oil Chem. Soc., 46 (1969) 537, as described on pages 8-11 of the application. The branched alcohol sulphates were tested against multisebum or triolein soiled permanent press 65/35 polyester/cotton (PPPE/C) fabric. The formulation in each case was 0.2 g/L alcohol sulphate, 0.34 g/L builder (Zeolite-4A) and 0.2 g/L Na_2CO_3 .

The results, expressed as % soil removal, are presented in the following Tables 1 and 2.

Table 1

Effect of 2-alkyl branched alcohol sulphates on multisebum soil removal

Branching	<u>15-Carbon alcohol sulphate</u>		<u>16-Carbon alcohol sulphate</u>	
	tested at 10 °C	tested at 32 °C	tested at 10 °C	tested at 32 °C
Methyl	17.6	---	17.6	38.3
Ethyl	---	---	14.0	34.1
Propyl	12.4	31.1	---	---
Butyl	---	---	6.7	32.9
Hexyl	4.0	7.3	7.5	13.4

LSD₉₅ (Least Significant Difference at 95% probability) is 2.0 at 10 °C and 4.8 °C at 32 °C

Table 2

Effect of 2-alkyl branched alcohol sulphates on triolein soil removal

Branching	<u>14-C alcohol sulphate</u>		<u>15-C alcohol sulphate</u>		<u>16-C alcohol sulphate</u>	
	at 10 °C	at 32 °C	at 10 °C	at 32 °C	at 10 °C	at 32 °C
Methyl	---	---	---	---	21.4	34.7
Hexyl	3.5	5.2	4.8	13.2	7.5	16.0

LSD₉₅ (Least Significant Difference at 95% probability) is 4.3 at both temperatures

Attachment B

59th Southwest Regional Industrial Innovation Awards Program

October 25 – 28, 2003
Oklahoma City, OK

Honoring Successful Innovations from the Chemical Enterprise



Because the innovations of industry are essential to a healthy economy, the American Chemical Society's (ACS's) Industry Member Programs has instituted the Regional Industrial Innovation Awards Program. The program recognizes individuals and teams for their creative innovations that have resulted in a commercial product or process. This awards program also highlights the outstanding contributions that the profession of chemistry has given to society, as well as the corporate leadership that encouraged the dissemination of knowledge that is facilitated in these innovations.



The recipients of the 59th Southwest Regional Industrial Innovation Awards Program are **Mr. Louis Kravetz, Dr. Brendan D. Murray, and Dr. David M. Singleton** (Shell Chemical LP, Houston, TX) for developing a new class of high solubility, biodegradable alcohol-based surfactants with selective and controlled degrees of branching for use in cold water washing processes.

Mr. Louis Kravetz joined Shell Chemical Co. in 1963 after receiving his M.S. in chemistry from the Brooklyn Polytechnic Institute. During his 35 year career at Shell, he worked at three different research facilities – Union Labs, NJ, Emeryville, CA, and Westhollow Technology Center, Houston, TX. During this time, he has worked on applications research in textiles, hydrogen peroxide, glycerine, ethylene glycol, and surfactants. Mr. Kravetz is the recipient of 14 U.S. patents and is the author of 34 technical publications.

Dr. Brendan D. Murray received his B.A. in chemistry from the University of California, Santa Cruz in 1980 and his Ph.D. in inorganic chemistry from the University of California, Davis in 1984. He joined Shell Development Co., Houston, TX in 1985 and was an exchange scientist from 1995–1996. Dr. Murray returned to Shell's Westhollow Technology Center in Houston, TX in 1996 and continued to develop new commercial applications for catalysis where he is currently the Catalyst Opportunity Development Strategist. He is the recipient of 26 U.S. patents and has authored over twenty technical presentations.

Dr. David M. Singleton received his B.S. in chemistry from Queen Mary College, London University in 1960, his Ph.D. in physical-organic chemistry from McMaster University in Hamilton, Ontario in 1965, and his postdoctoral studies at Case Institute of Technology in 1967. Dr. Singleton joined Shell Development Co., Emeryville, CA in 1967 and was an exchange scientist in Amsterdam, The Netherlands from 1975–1976. Dr. Singleton returned to Shell's Westhollow Technology Center in 1976 where he worked on a number of challenging issues in the areas of catalysis and household detergents. Dr. Singleton retired from Shell in 1999 after 32 years.

Join us in honoring Mr. Kravetz, Dr. Murray, and Dr. Singleton. The program will include a symposium in which the honorees will present his outstanding work and an awards ceremony in which the honorees will be formally recognized. This industrial-focused event also presents a significant networking opportunity for ACS members, industrial researchers, corporate leaders, and students.

Symposium

Monday, October 27, 2003
(Time/Location – TBD)

Awards Ceremony

Monday, October 27, 2003
6:30 – 8:30 p.m.
(Location – TBD)

For more information regarding the Regional Industrial Innovation Awards Program, please contact
Ms. Vanessa L. Johnson-Evans, American Chemical Society, 1155 Sixteenth Street, NW, Washington, DC 20036;
202-872-4373; 1-800-227-5558, ext. 4373; www.chemistry.org/industry/regionalawards.

Attachment C



Shell Chemicals

The Development and Commercialization of Biodegradable Selectively Branched Detergent Alcohols

Louis Kravetz, David Singleton and Brendan Murray*

Shell Chemical LP

Westhollow Technology Center

Houston, TX 77082



Shell Chemicals

Surfactants

Multi-million ton/ year global business

Anionic surfactants are the largest group

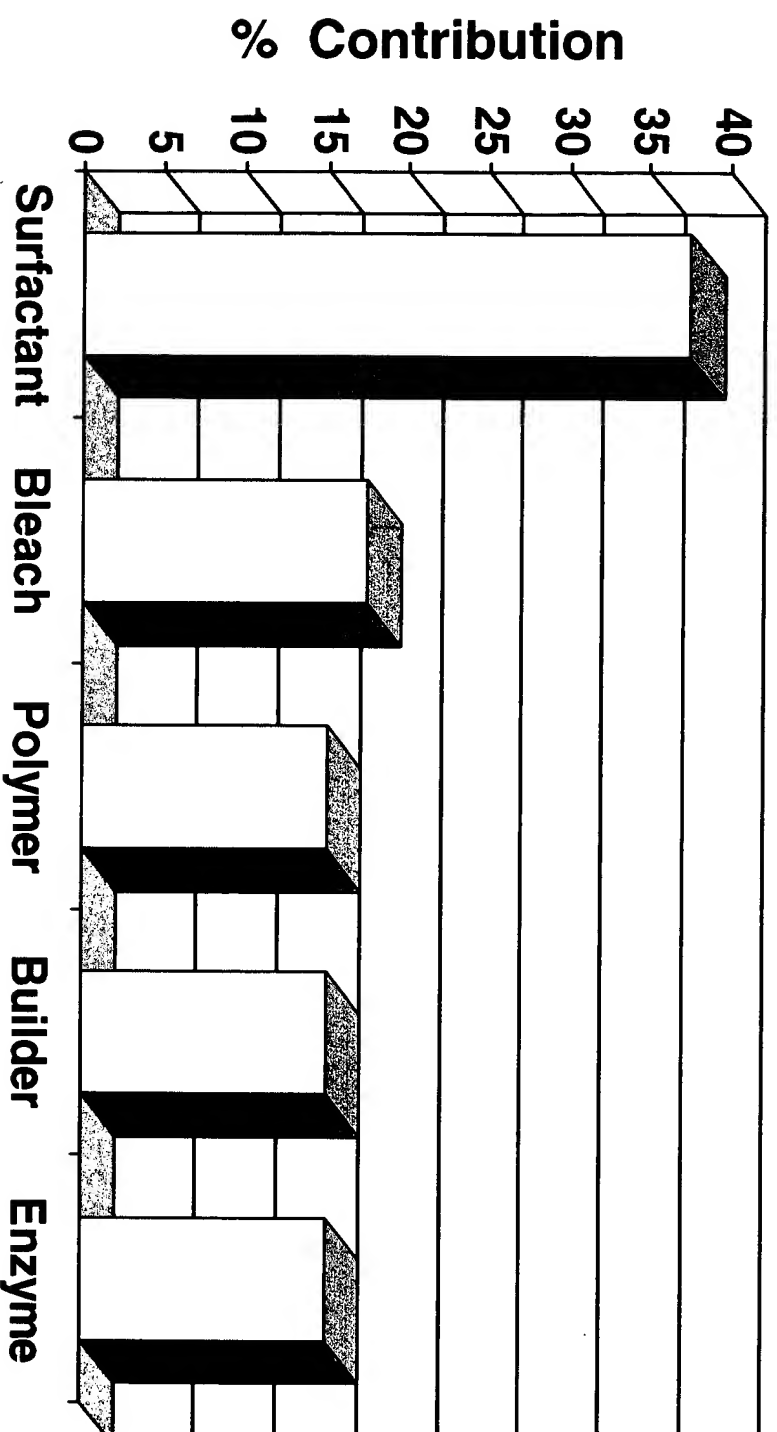
They wet fabrics and soils; remove dirt and stains

The single most important cleaning ingredient in most laundry and household cleaning products



Shell Chemicals

Performance Contribution to Detergency

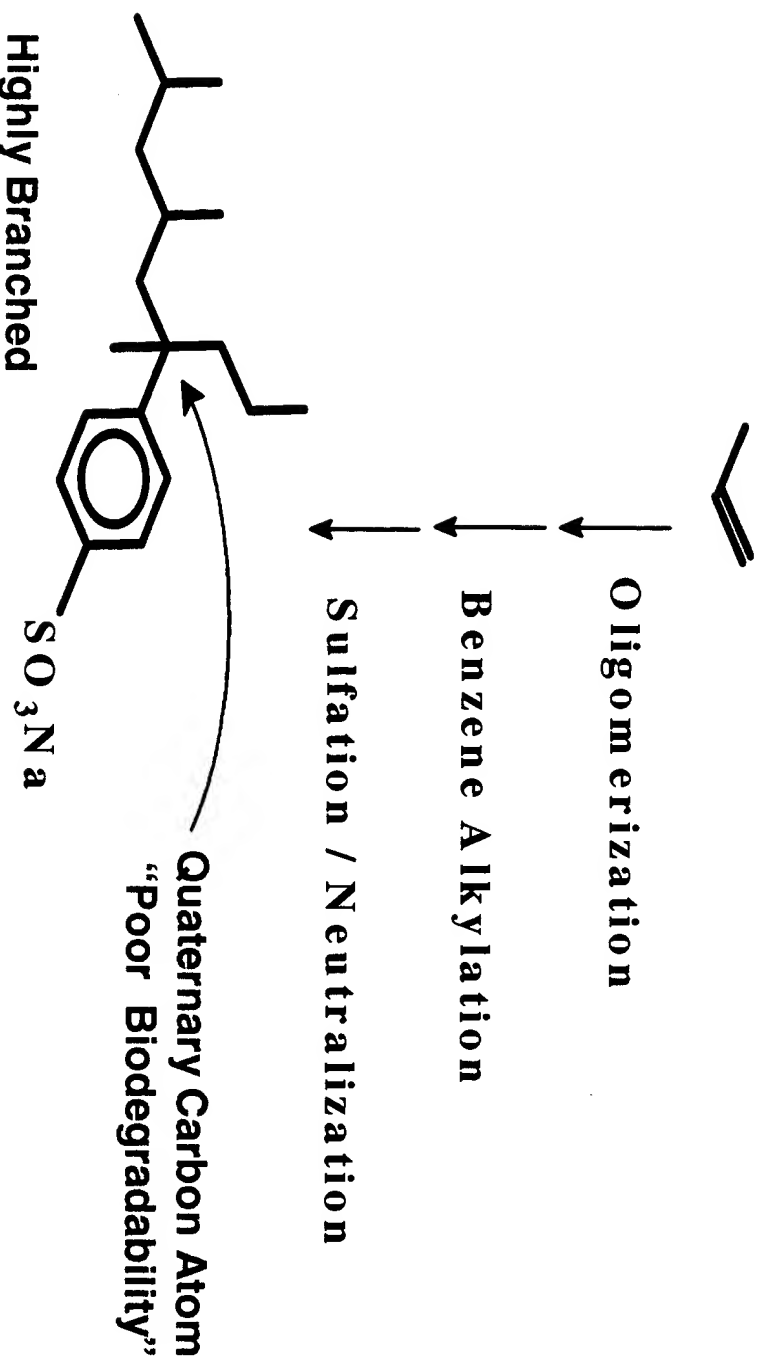


* G. Bailliey et al., *Proceedings of the 5th World Conference on Detergents*, (2003)



Shell Chemicals

1950's Vintage Alkylbenzene Sulfonate





Shell Chemicals

Surfactant Events – A Need for Innovation

1950's - Highly Branched Alkylbenzene Sulfonates, (ABS)

slow biodegradation, foaming, aquatic toxicity?

1960's – ABS Regulation begins – Rapid replacement by Biodegradable Linear Alkylbenzene Sulfonates, Linear Alcohol Sulfates and Linear AES

A Paradigm is born: “*Alkyl branching is Bad*”

1970's - Movement to lower wash temperatures creates a need for better cold water detergency

1980's *The Alkyl Branching Paradigm is Challenged*

2000's - High Solubility Biodegradable, Selectively Branched Detergents are commercialized



Shell Chemicals

Recent Trends in Washing Processes

- **Lower Wash Water Temperature**
- **Lower Energy Consumption**
- **Shorter Wash Times**
- **Reduced Water Usage**

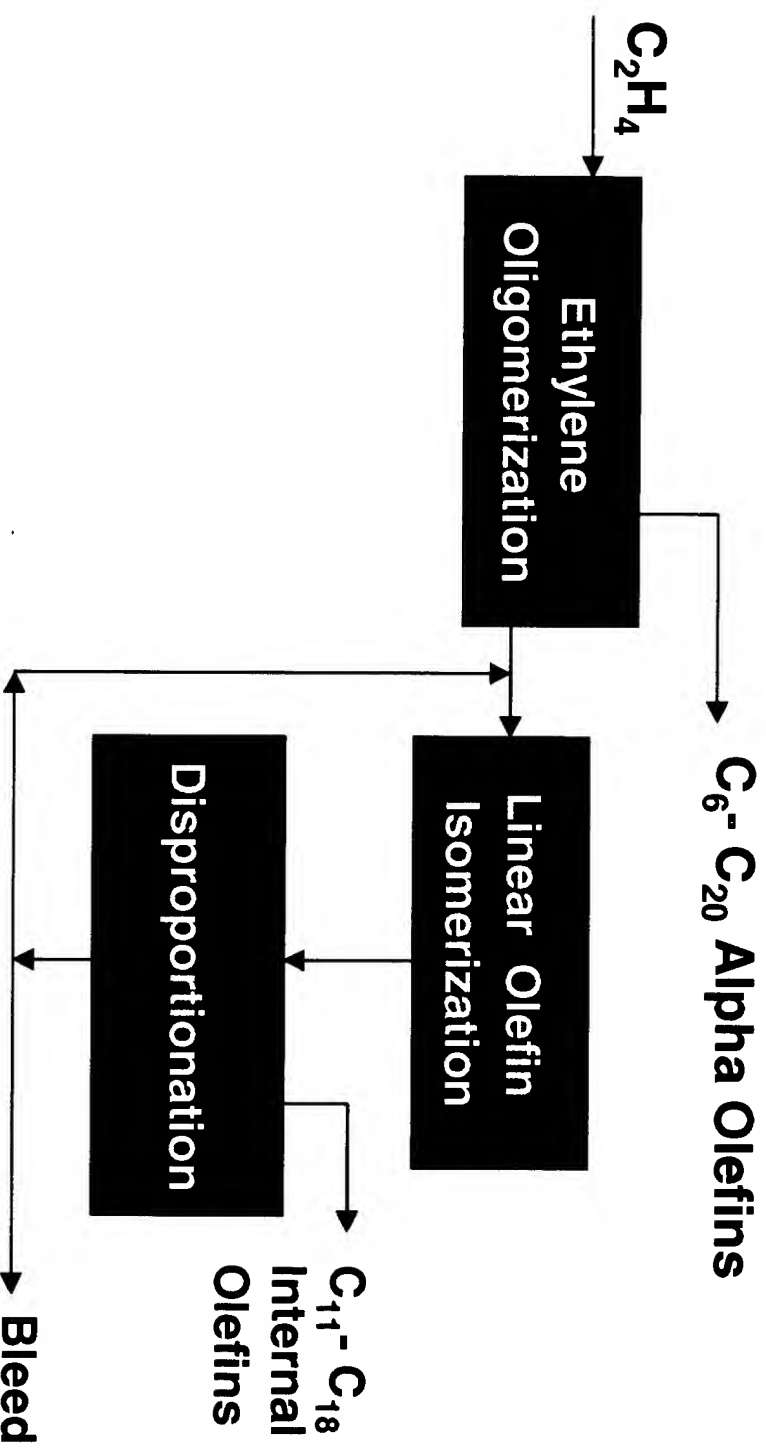


Shell Chemicals

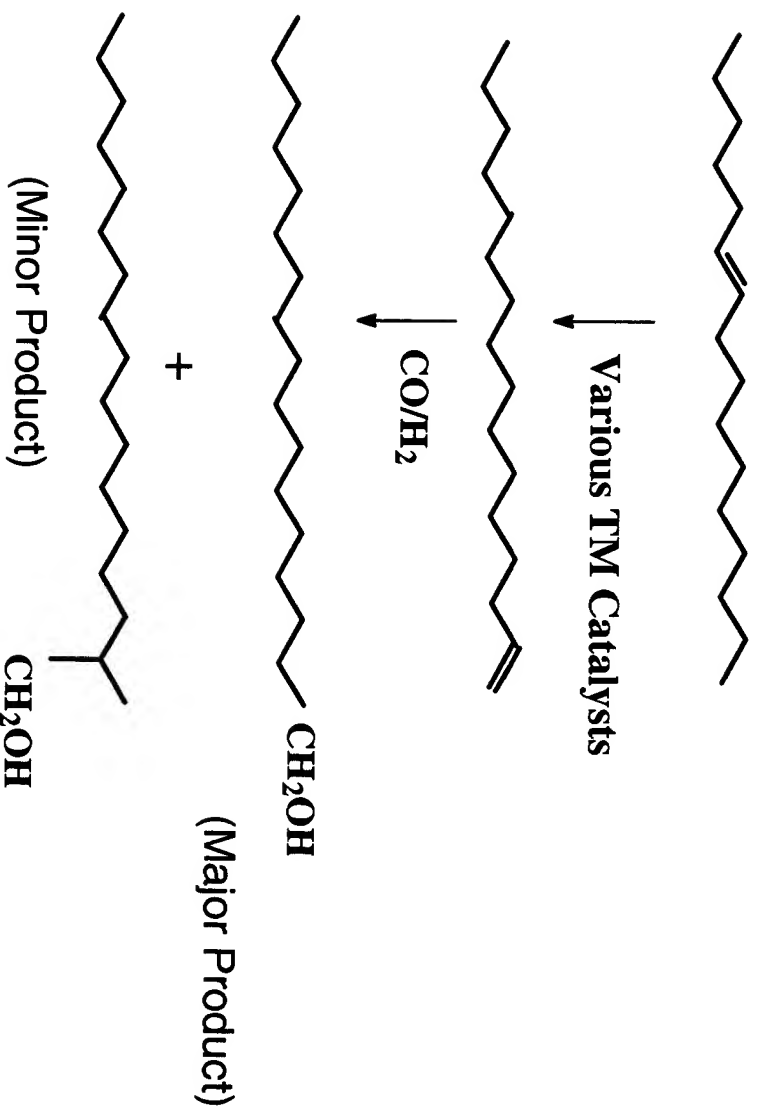
Desired Surfactant Properties

- **Excellent Surface Activity**
- **Readily Biodegradable**
- **Superior Cold Water Detergency**
- **Improved Hard Water Solubility**
- **Ability to use Less Surfactant**
- **Affordable and Consistent Production**

Shell Higher Olefins Process (SHOP)



Shell Hydroformylation Process (SHF)





Model Compound Studies

Malonic Ester Synthesis of 2-Alkyl Branched Alcohols



Alcohols were converted to the alcohol sulfate sodium salts by treatment with $ClSO_3H$, followed by neutralization with $NaOH$



Shell Chemicals

How to Introduce Controlled Branching

Controlled Dimerization / Oligomerization of Lower Olefins

Cross Metathesis Schemes

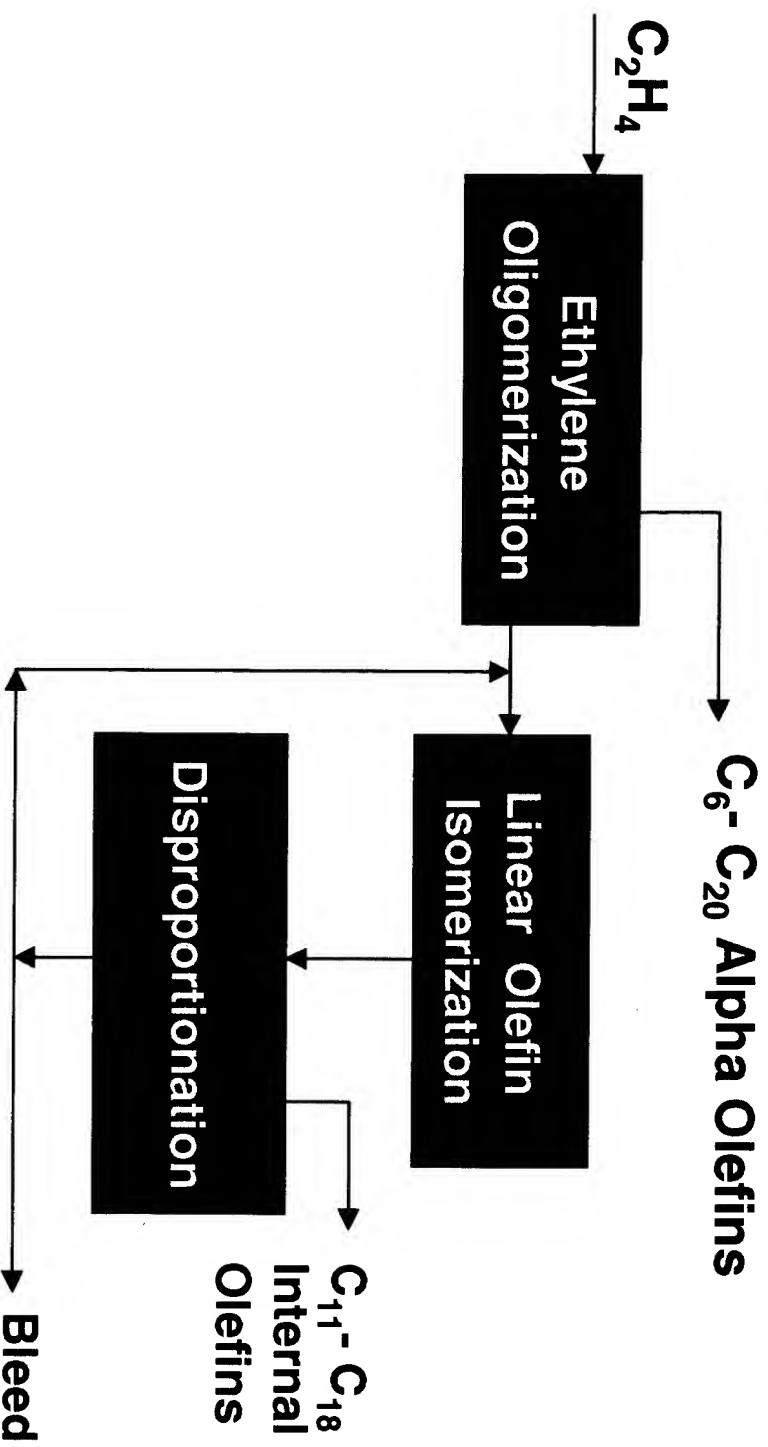
Selective Skeletal Isomerization of Linear Olefins

- Use a proprietary, “pore engineered” zeolite catalyst
- Makes mainly mono-branched olefins with the alkyl groups distributed at beneficial positions along the backbone
- Very low level of quaternary carbon atoms in product



Shell Chemicals

Shell Higher Olefins Process (SHOP)



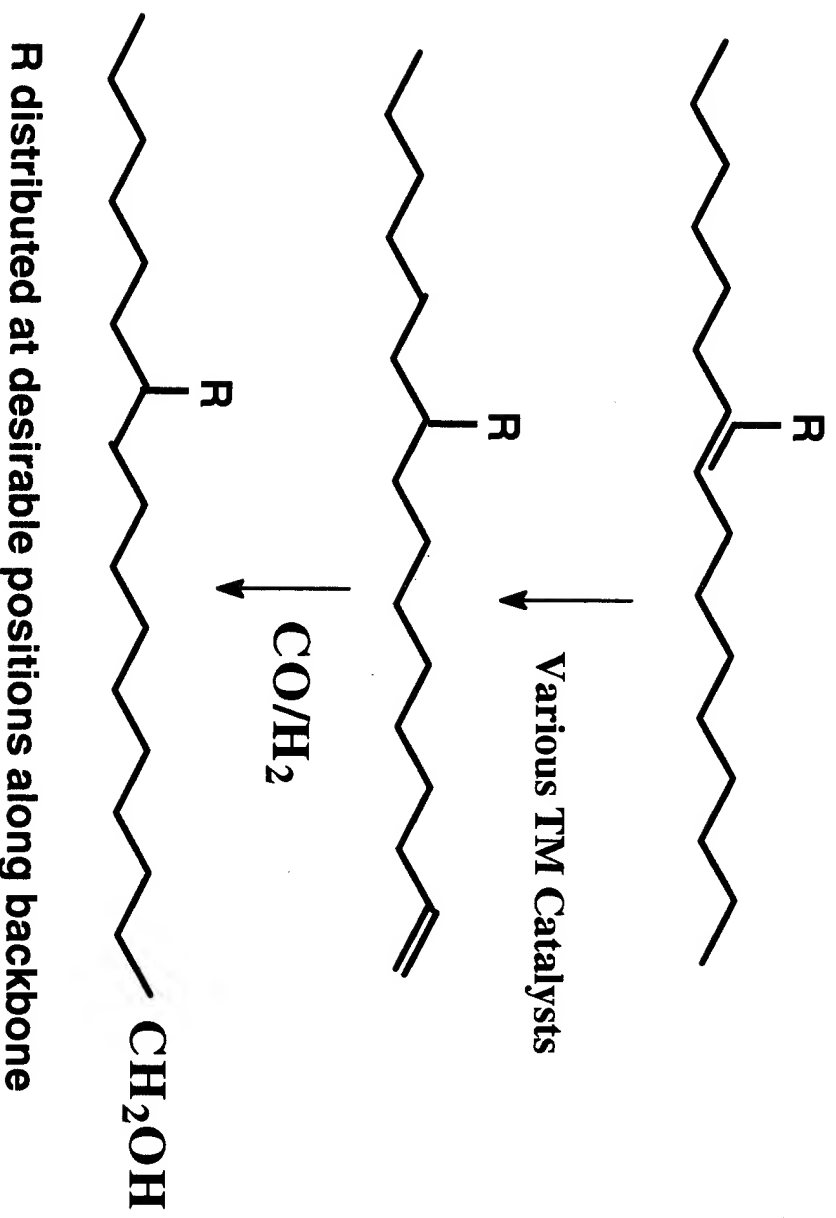


Shell Chemicals

Skeletal Olefin Isomerization Process

- Uses Alpha or Internal Olefins as Feedstocks
- Low Severity Operation
- Thermodynamic Equilibrium Conversion (>95%)
- Very High Selectivity (>98%)
- Multiply Regenerable Zeolite Catalyst
- Fully Compatible with the SHOP and SHF Processes
- Very High Catalyst Turnover Rate

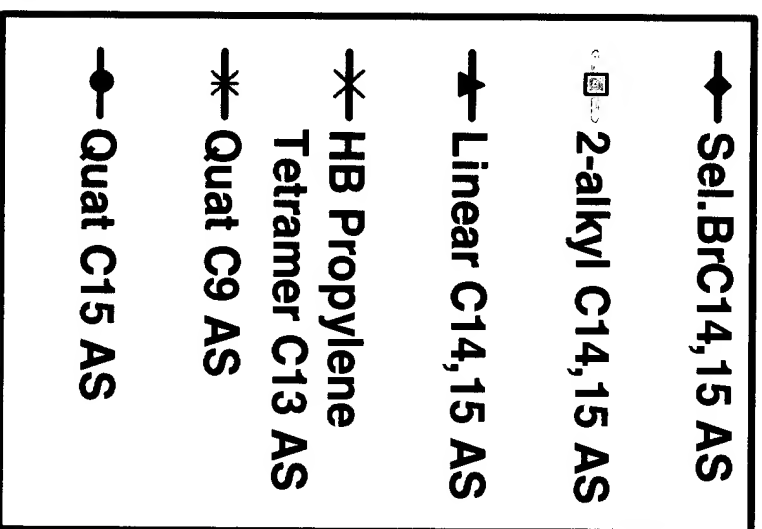
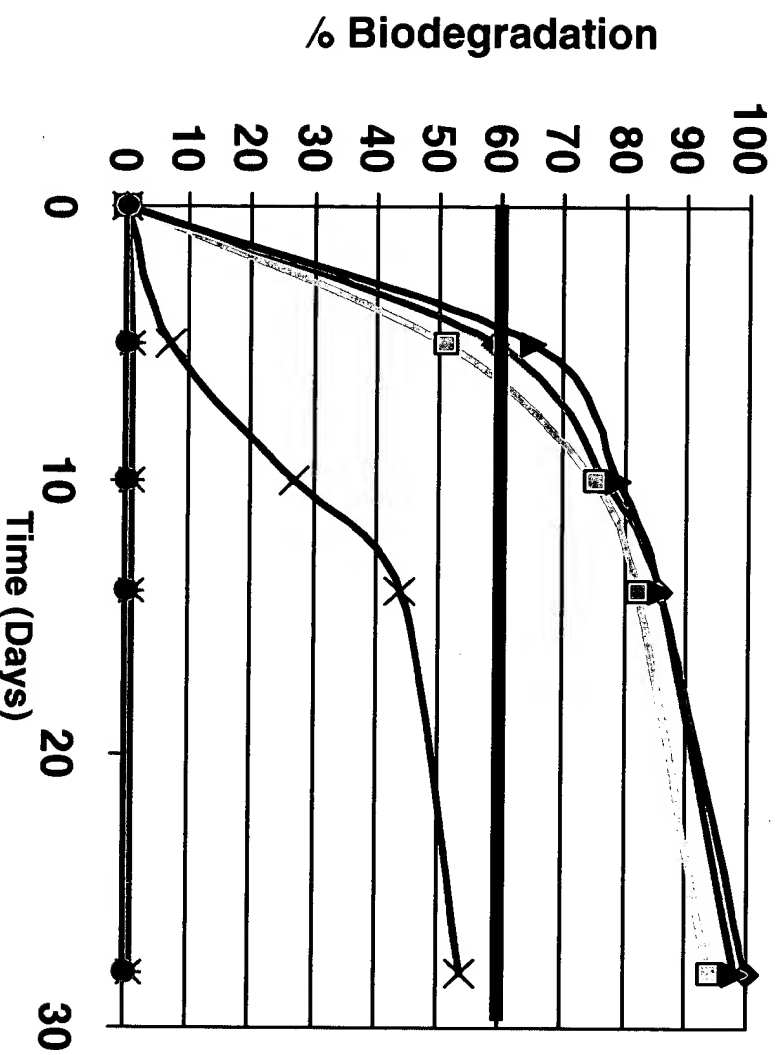
Shell Hydroformylation Process





Shell Chemicals

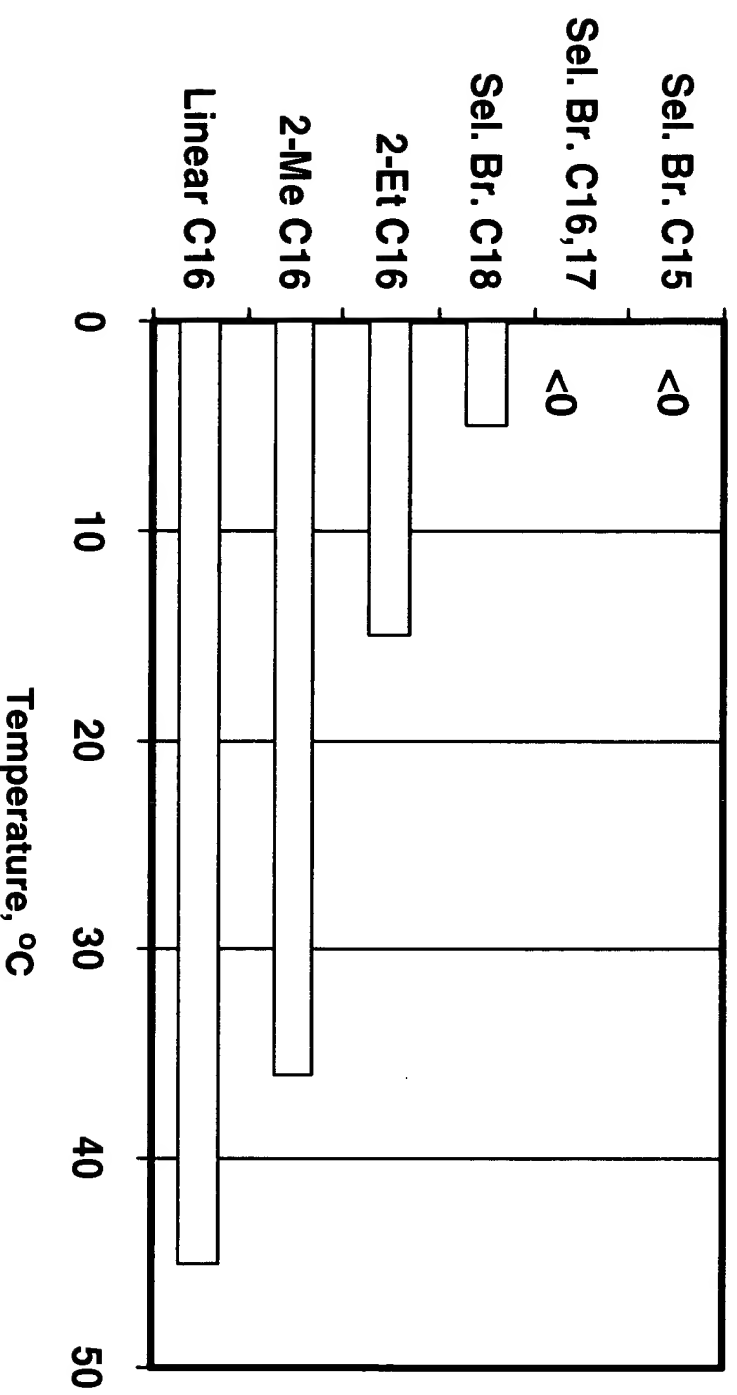
Closed Bottle Biodegradation Results for Various Alkyl Alcohol Sulfates





Shell Chemicals

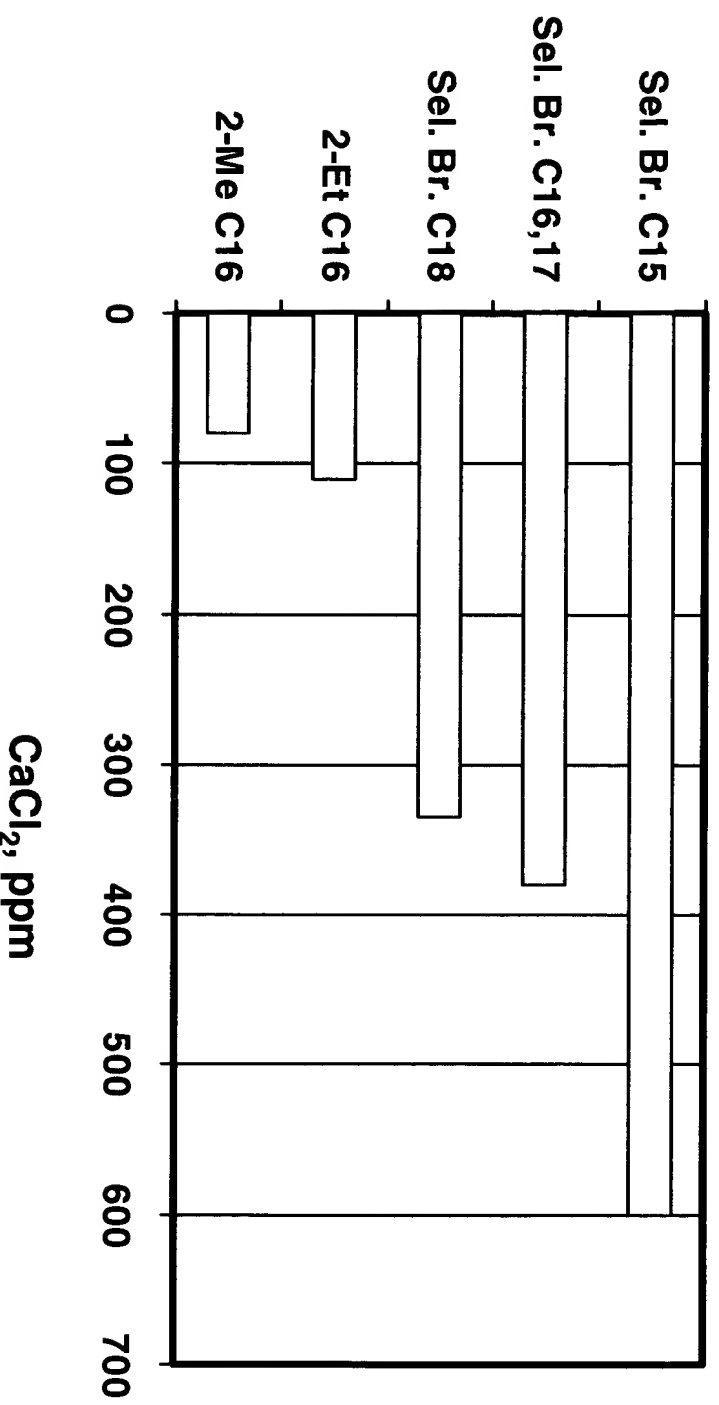
Krafft Temperature of the new Selectively Branched Alcohol Sulfates





Shell Chemicals

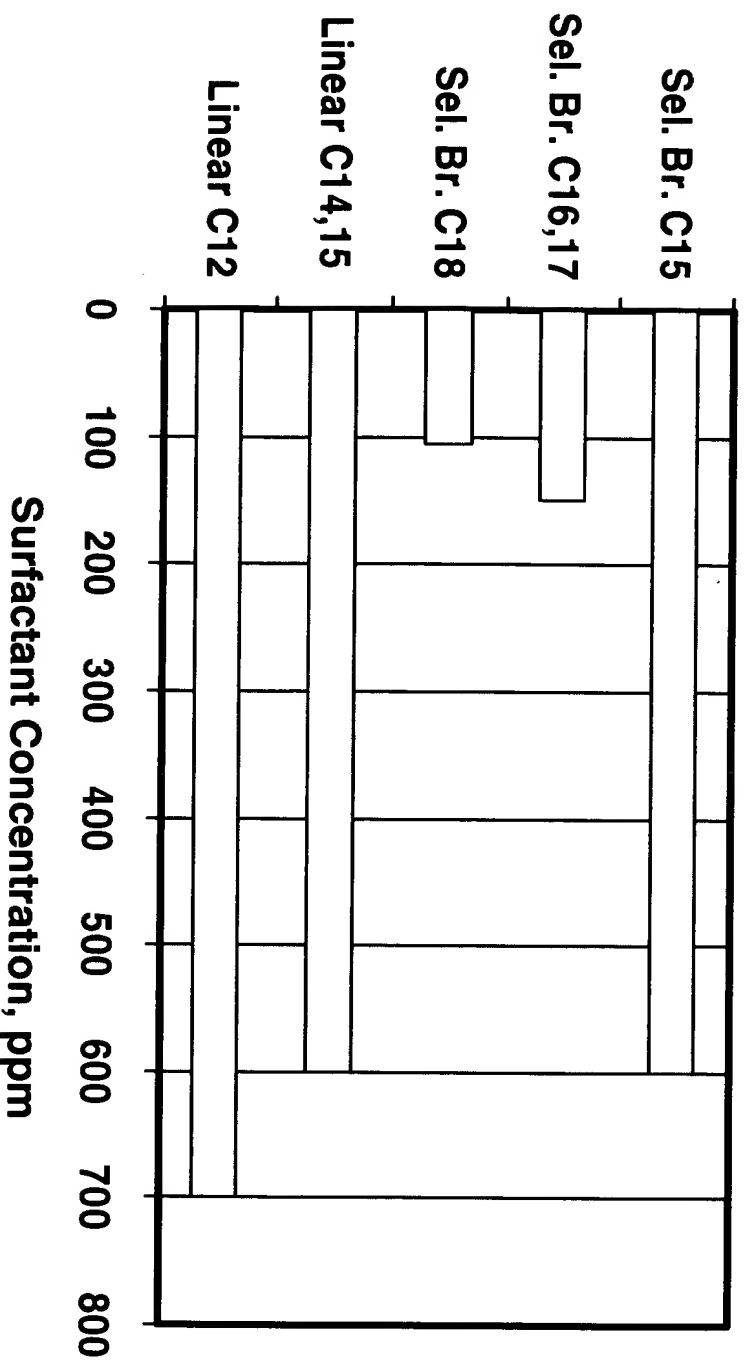
Calcium Tolerance of the new Selectively Branched Alcohol Sulfates





Shell Chemicals

Critical Micelle Concentration of the Selectively Branched Alcohol Sulfates

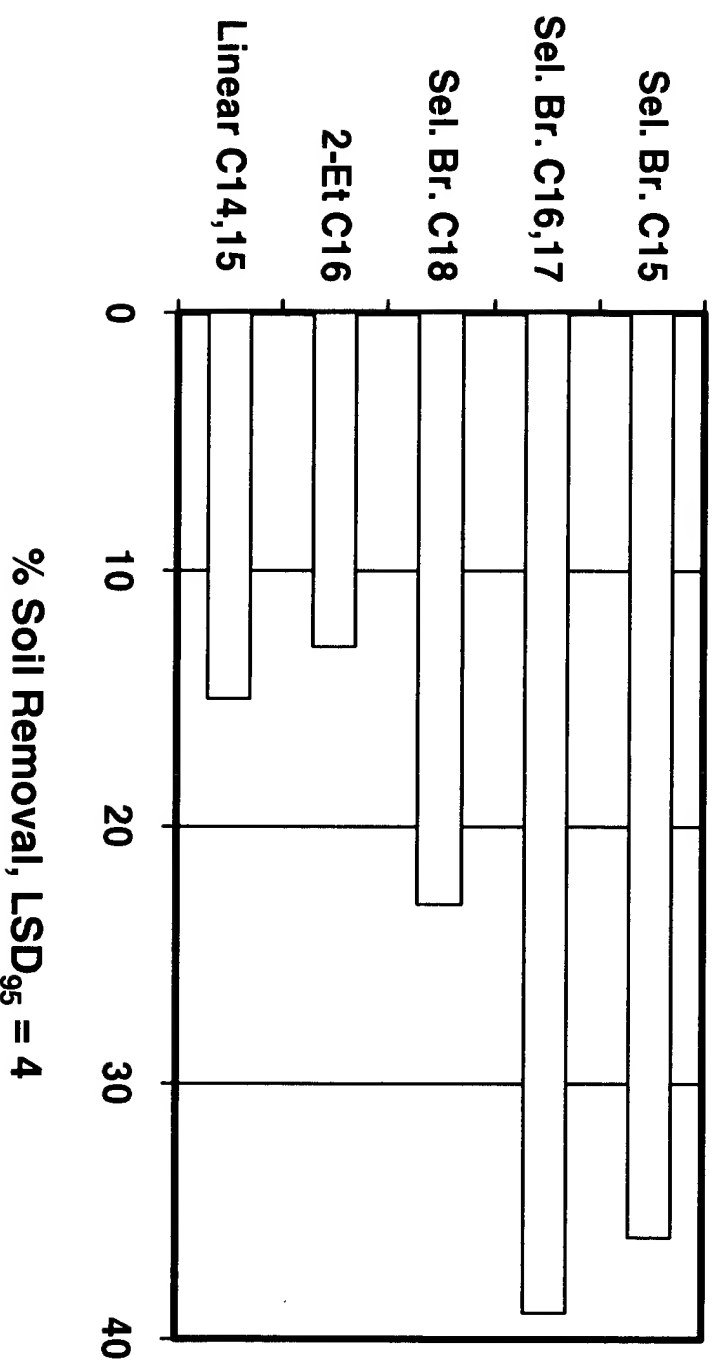




Shell Chemicals

Detergency Performance of the new Selectively Branched Alcohol Sulfates

(at 10°C and 150 ppm Water Hardness)

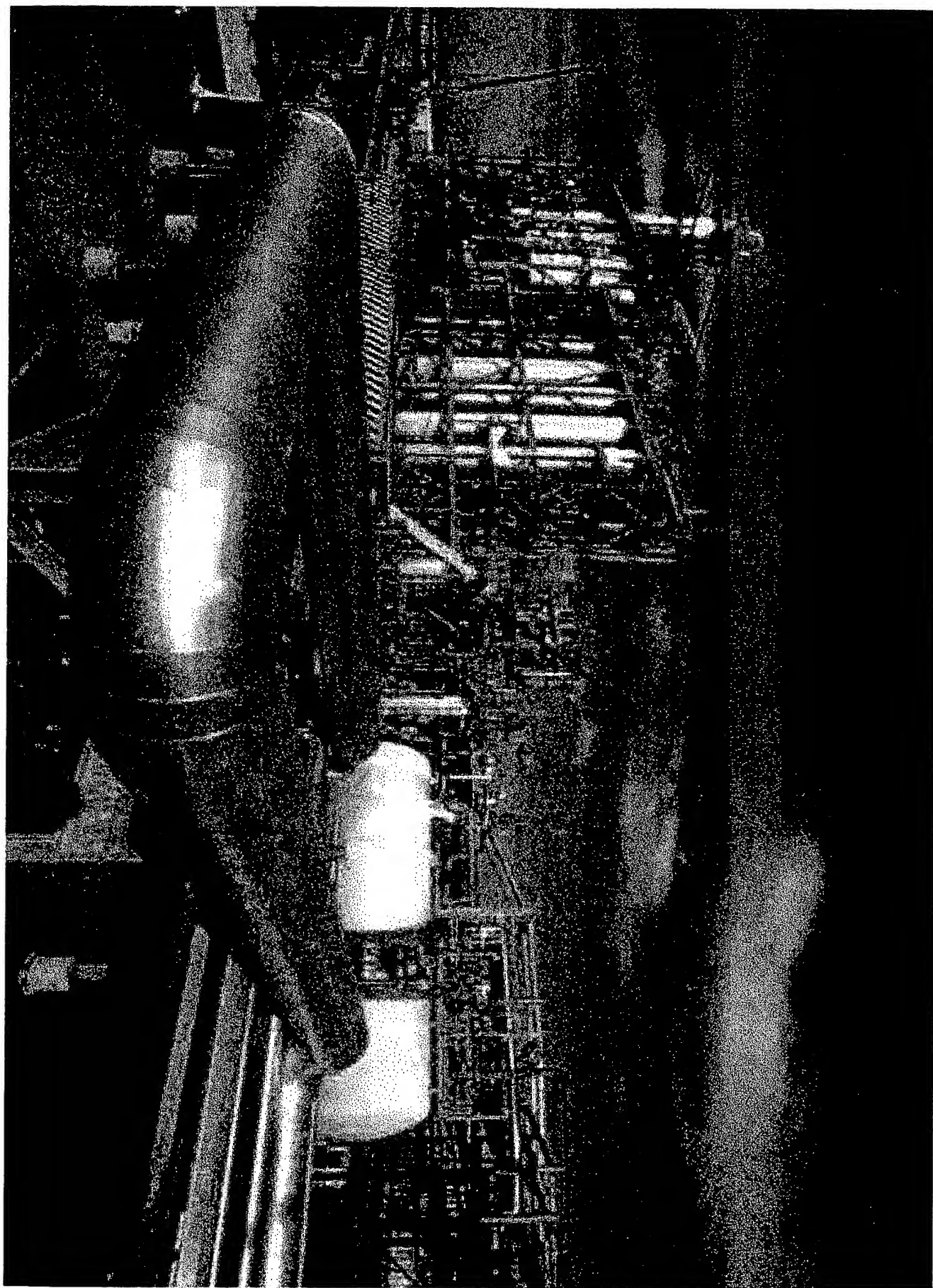




Shell Chemicals

Partnering with Procter & Gamble

- P&G is a **Leading Global Supplier** to the Detergent Industry
- P&G conducted independent studies that pointed to a Primary Alcohol with a single methyl branch near the middle of the chain
- Evaluated various Shell “Selectively Branched” Alcohols
- Derivatized and formulated products based on the new alcohols
- A joint decision was made to commercialize the Innovation





Shell Chemicals

Commercialization

- Product was scaled up in several stages (6, 50 and 3700 tonnes)
 - Allowed Process Modeling and Design Optimization
 - Customer feedback
- P&G worked closely with Shell during the Process
 - HS&E Studies, Alcohol Conversion and Product Formulation
 - Logistics, Product Specifications
 - Market Development Work
- World-Scale Olefin/Alcohol Plant built at Geismar, LA. in 2001
 - On spec product produced within 12 hours of feed-in
 - Breakthrough Technology Confirmed in Operations
- Alcohols successfully formulated into Quick Dissolving Tide®

“Tide is the most popular laundry detergent used in the USA”



Shell Chemicals

New Opportunities

■ Personal Skin Care Products

- Excellent Emollient / Moisturizer
- Non-oily
- Good Viscosity and Solubility Characteristics
- Biodegradable

■ Industrial Fluids

- Low Pour Point
- Good Stability

■ Chemical Intermediates

- Novel Composition
- Reagent for Various Industries



Shell Chemicals

Acknowledgements

- The American Chemical Society
- Procter & Gamble
- Zeolyst International / CRI Catalyst Inc.
- Shell Chemical
 - GOAL Team - B. Colquhoun, B. Klein, P. Spicer, S. Sumrow
 - Geismar Plant and Engineering Staff
 - Scale-Up - B. Adkison, P. Ayoub, L. Gingrich, T. Hoewing, D. O'Neal
 - HODer - L. Fenouil, D. Haseltine, D. Johnson, S. Papitto, W. Schmidt, T. Thomason
 - Catalysis - B. Gambhir, D. Hamilton, B. Winqvist
 - D. Holecek, VP Technology – Americas
 - F. Keeth, President - Shell Chemical LP

Attachment D



FIRENZE

5th WORLD SURFACTANTS CONGRESS

May 29 - June 2, 2000
Fortezza da Basso
Firenze

PROCEEDINGS Volume 2



Comité Européen
des Agents d Surface

FEDERCHIMICA
Assobase - P.I.T.I.O.

Produttori Italiani
di Tensioattivi

SOLUTION AND PERFORMANCE PROPERTIES OF NEW BIODEGRADABLE HIGH-SOLUBILITY SURFACTANTS

W. Warren Schmidt, David M. Singleton, and Kirk H. Raney
Shell Chemicals

Abstract

Phase behavior, surface activity, and cleaning performance of biodegradable anionic and nonionic surfactant derivatives of long-chain alcohols have been studied. A tailored hydrophobe structure, which can be obtained through selective skeletal-isomerization of linear olefins followed by hydroformylation, provides enhanced cold-water solubility and improved water hardness tolerance as compared to conventional predominantly linear alcohol sulfates of comparable molecular weight. The impact of the structure on ethoxylated nonionic surfactant properties is less pronounced, although differences in physical properties such as pour point and gel formation are noted when compared to linear alcohol ethoxylates. Results of radiotracer detergency studies performed in a Terg-O-Tometer confirm the positive attributes of the high-solubility surfactants. This class of surfactant may permit advances in the consumer laundry process viewed from a full lifecycle perspective by enabling high cleaning performance under conditions favoring an improved environmental profile.

Résumé

Le comportement de phases, l'activité de surface et le pouvoir nettoyant des dérivés tensioactifs anioniques et non ioniques ont fait l'objet d'une étude. Une structure hydrophobe spécialement adaptée, qui peut être obtenue par l'intermédiaire de l'isomérisation squelettique des oléfines linéaires, suivie de l'hydroformylation, fournit une plus grande solubilité par temps froid et une meilleure tolérance de la dureté de l'eau, par rapport aux sulfates d'alcool conventionnels principalement linéaires dont le poids moléculaire est comparable. L'impact de la structure sur les propriétés des agents tensioactifs non ioniques éthoxylés est moins marqué, bien que des différences soient observées dans les propriétés physiques, telles que le point d'écoulement et la formation de gel, par rapport aux éthoxylats d'alcool linéaire. Les résultats des études de détergence au traceur radioactif effectuées dans un "Terg-O-Tometer" confirment les attributs positifs des agents tensioactifs de haute solubilité. Cette classe d'agents tensioactifs pourrait permettre de faire des progrès au niveau du processus de blanchissage de consommation, si on le considère du point de vue d'un cycle de vie complet, sous des conditions qui favorisent un meilleur profil environnemental.

Zusammenfassung

Es wurden Phasenverhalten, Grenzflächenaktivität und Reinigungsleistung biologisch zersetzbarer anionischer und nichtionisierender Tensidderivate untersucht. Eine genau abgestimmte wasserabweisende Struktur, die durch eine besonders gewählte Skelett-Isomerisierung linearer Olefins und einer nachfolgenden Hydroformylierung gebildet wurde, bietet eine erhöhte Kaltwasserlöslichkeit und bessere Wasserhärte-toleranz als herkömmliche und meistens lineare Alkoholsulfate eines vergleichbaren Molekulargewichts. Der Struktureinfluß auf die Eigenschaften ethoxylierter nichtionisierender Tenside ist weniger ausgeprägt, obwohl Unterschiede in den physikalischen Eigenschaften wie Pourpoint und Gelbildung im Vergleich mit linearen Alkoholethoxylaten zum Vorschein kommen. Mit den Ergebnissen von Radionuklid-Untersuchungen in einem Terg-O-Tometer wurden die positiven Merkmale der Tenside mit hoher Löslichkeit bestätigt. Aus der Sicht einer Voll-Lebenskreislauf-Perspektive unter Bedingungen, die ein verbessertes Umweltsprofil begünstigen, kann diese Tensidgruppe zu einem Fortschritt des Verbraucher-Wäschereiprozesses führen.

INTRODUCTION

Branched alcohols are an important constituent of many high volume synthetic detergent alcohols made using the Oxo process (1). In separate work, it was shown that the separated branched fraction of certain synthetic alcohols exhibited an excellent biodegradation profile (2). It was obviously of interest to document the effect of specific alcohol branching on the surfactant properties of alcohol sulfates. Additionally, random mono-methyl alcohols were synthesized, and physical chemistry and laboratory cleaning evaluations conducted.

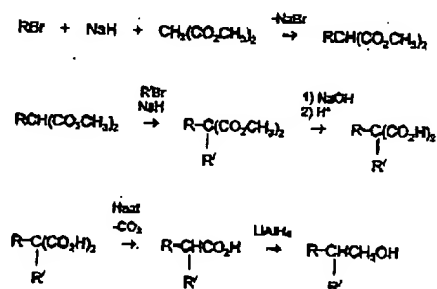
Early German workers used laboratory organic synthesis to make a limited series of alcohols and sulfates (3). For this research, two versatile synthetic schemes were adapted to a wide range of compounds, and the performance testing was likewise modified to reflect current practice including lower wash temperatures.

EXPERIMENTAL

General Methods for Synthesis: As depicted in Figure 1, a variety of alcohols were synthesized by

Figure 1

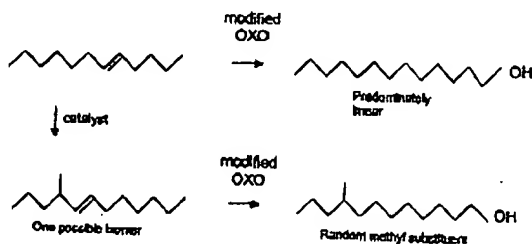
Malonic Ester Synthesis of 2-Alkyl Branched Alcohols



alkylation of malonic ester (4). With this method, alcohols with a total of C-12 to C-18 were made, and 2-alkyl branches from C-1 to C-6 were incorporated. Figure 2 shows the two-step procedure for introducing random mono-methyl branching into an alcohol (5). The alcohols were > 97% pure. All ClSO_3H , followed by neutralization with NaOH (6).

Figure 2

Random Methyl Alcohol Synthesis



Krafft Temperatures of Alcohol Sulfates: Aqueous 1% surfactant solutions were frozen, and the solutions were allowed to slowly warm. The reported Krafft temperature is the temperature where the solution was fully transparent.

Calcium Tolerance: Aqueous surfactant solutions were made at a concentration of 0.06% weight, and adjusted to a pH of approximately 9 with 1% NaOH. The surfactant solutions were warmed to 40 °C. Aliquots of 10% CaCl_2 were added, and the surfactant which remained dissolved in the upper (clear) layer was determined via the two phase titration method (7). The reported calcium tolerance is amount of CaCl_2 which must be added to precipitate 50% of the anionic surfactant.

The random mono-methyl C-16,17 alcohol was ethoxylated with an average of nine ethylene oxide groups using standard KOH ethoxylation. For comparison, a nine-EO ethoxylate with a linear C-16 hydrophobe was prepared by blending ethoxylates obtained from Uniqema. Also studied were the seven-EO ethoxylates obtained through standard ethoxylation of the linear and branched fractions of a predominately linear C-14,15 alcohol.

The cloud point and Krafft temperature of 1% aqueous alcohol ethoxylate solutions were measured in deionized water using dipping probe turbidimetry (8,9). Solutions were first chilled overnight in a freezer at -5°C. The solutions were then heated at a rate of about 1°C/minute in a jacketed beaker with agitation provided by a Glas-Col® non-aerating stirrer at 3000 rpm. Turbidity was determined by measuring the light transmittance through the solution at 650 nm. The first temperature where complete clearing of the solution occurred was taken as the Krafft temperature while the higher temperature at which turbidity reappeared due to formation of a dispersed phase was taken as the cloud point.

Solution Time Method: The solution times of the neat ethoxylates were measured by injecting 0.20 cc of liquid surfactant into 50 cc deionized water in a flat bottom pour point tube (Corning No. 6900). The water was stirred at 500 rpm with a 1.5 cm x 0.5 cm magnetic stirring bar. The times for complete surfactant dissolution were measured at 25°C with the temperature of the sample being controlled by placing the pour point tube in a thermostatically-controlled water bath. Measurements were performed in duplicate and averaged.

Alcohol Ethoxylate Pour Points: Pour points for the commercial C-14,15 samples were obtained using method ASTM D97-85 with an automatic pour point apparatus. Visual determination of pour points was made for the other samples by observing their flow behavior as 50 cc were slowly warmed in a water bath.

Surface Tension: Equilibrium surface tension as a function of surfactant concentration was measured at 25°C using an automated Lauda tensiometer. This instrument doses fixed increments of stock solution into 100 cc of deionized water that is contained in a thermostatically-controlled beaker. Equilibrium surface tension is measured automatically using the Du Nuoy ring method. From the surface tension-concentration plots, critical micelle concentration was determined by standard procedures (10).

Detergency: Multisebum soil removal was determined using the published laboratory radiotracer detergency procedure (11,12). All alcohol sulfates were evaluated in the following prototype formulation: 0.2 g/L anionic, 0.34 g/L zeolite, and 0.2 g/l of Na_2CO_3 .

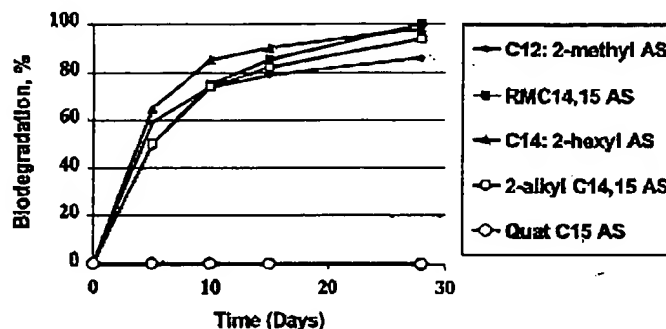
Biodegradation: A laboratory estimation of biodegradation was conducted by an adaptation of the CO_2 evolution method of Sturm (13)

DISCUSSION

• Biodegradation

A screening study of biodegradation was used to compare a variety of alcohol sulfates. As depicted in Figure 3, only a surfactant synthesized to contain a quaternary carbon atom failed to evolve CO₂ at a

Figure 3
Closed Bottle Biodegradation Results for 2-Alkyl Alcohol Sulfates



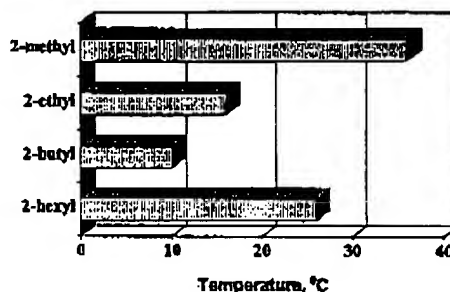
rapid rate. A variety of 2-alkyl branches or a random mono-methyl substituent all performed equally well in this screen. This result was at least in part predicted by the previous work from Shell (2).

• Surfactant Properties of 2-Alkyl Alcohol Sulfates

Displayed in Figure 4 are the Krafft temperatures of branched C-16 alcohol sulfates. With this series of alcohol sulfates, the minimum in Krafft temperature occurs with the attachment of a 2-butyl group. The all linear hexadecanol sulfate has a Krafft temperature of 45 °C (14).

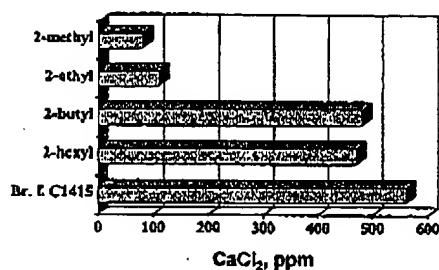
Figure 4

Krafft Temperature of C16: 2-Alkyl Branched Alcohol Sulfates



The calcium tolerance of this series of C-16 alcohol sulfates is depicted in Figure 5. The methyl and ethyl derivatives are approximately equal, while either butyl or hexyl introduce the greatest solubility.

Figure 5
Calcium Tolerance of C16; 2-Alkyl
Alcohol Sulfates

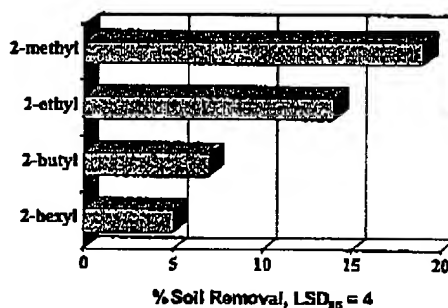


- Detergency Evaluation of 2-Alkyl Alcohol Sulfates

In 1969 Götte and Schwuger (3) reported the reflectance detergency of branched C-16 alcohol sulfates at 40 °C. It was noted that the 2-methyl branched alcohol sulfate gave the highest level of cleaning. With the availability of a broader selection of chain lengths, the generality of this observation has been investigated.

In this present work, C-16 alcohol sulfates were evaluated at 10 °C by an alternative radiotracer

Figure 6
Multisebum Detergency of C16 Alcohol
Sulfates: 10 °C and 150 ppm Water
Hardness



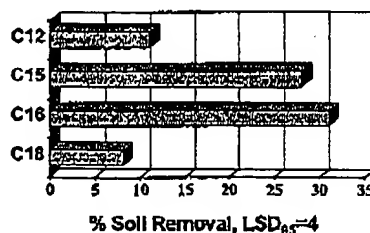
method, see Figure 6. Despite having the highest Krafft temperature and the lowest calcium tolerance, the 2-methyl derivative is the best performer, as observed by Götte and Schwuger (3). It is remarkable that the pattern was the same, since the temperature, soil, builder, and formulation are all different. This excellent activity is probably the result of greater surface activity of the 2-methyl surfactant. However, it is likely that the surfactant did not fully dissolve at the detergency conditions used here.

Additionally, a variety of total chain lengths, all with 2-methyl branches were evaluated, Figure 7. Performance is optimized for the C-16 total chain length, at the low temperature cleaning conditions utilized. It is presumed that the C-12 derivative has a relatively high cmc, and thus more surfactant would have been required. The C-18 material was poorly soluble, and therefore little surfactant was available at the conditions of this evaluation.

These surface chemistry and cleaning studies suggested that the length of the branch was an important variable in hydrophobe optimization. Exploratory chemistry yielded a way to synthesize alcohols with nearly exclusively methyl substituents (5).

Figure 7

Detergency Performance of 2-Methyl Branched Alcohol Sulfates 10 °C and 150 ppm Hardness

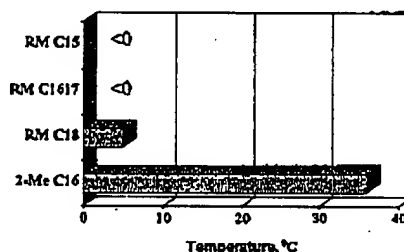


• Surfactant Properties of Random Methyl Alcohol Sulfates

Shown in Figures 8 and 9 are surfactant properties as a function of carbon content for the random methyl branched alcohol sulfates. Excellent cold water solubility is exhibited by all three RM samples

Figure 8

Krafft Temperature of RM Branched Alcohol Sulfates



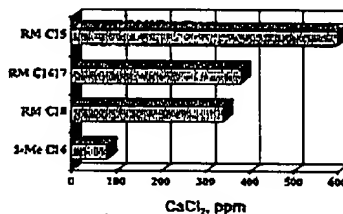
better
solubility
than

2 branched
only

as compared to pure 2-Me C16 alcohol sulfate which is not fully soluble at 1% concentration until heated to 36°C. Also, as shown in Figure 9, the random methyl systems exhibit much higher calcium tolerance than the 2-Me C16 alcohol sulfate.

Figure 9

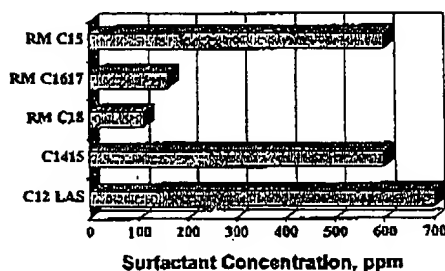
Calcium Tolerance of RM Branched Alcohol Sulfates



Critical micelle concentration values in deionized water for the RM sulfates at 25°C are compared in Figure 10 to values for a predominantly linear C1415 alcohol sulfate and C12 LAS. As expected, the RM alcohol sulfates having a high molecular weight exhibit quite low cmc's, indicative of low dosing requirements in laundry processes. Nevertheless, their Krafft temperatures are much lower than that for the commercial C1415 linear alcohol sulfate (37°C), and their calcium tolerance is much higher than

those for the C1415 sulfate and C12LAS, which are 40 ppm and 140 ppm, respectively. All three

Figure 10
Critical Micelle Concentration of RM
Branched Alcohol Sulfates

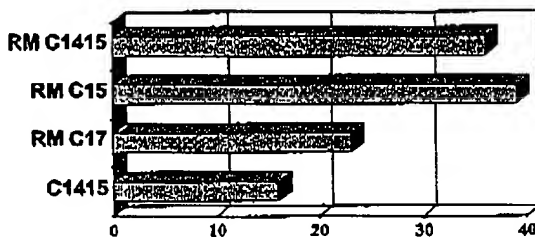


factors, low Krafft temperature, high calcium tolerance, and low cmc, are positive attributes of the random methyl alcohol sulfates which should contribute to excellent detergent properties, particularly in underbuilt systems at low washing temperatures.

- Detergency Evaluation of Random Methyl Alcohol Sulfates

Three different random-methyl alcohol sulfates were compared to a linear C-14,15 alcohol sulfate, Figure 11. Each of the randomly substituted alcohol sulfates was superior to the comparison surfactant.

Figure 11
Detergency Performance of RM Branched
Alcohol Sulfates
10 °C and 150 ppm Hardness



*better
detergency*

Random Methyl and 2-Alkyl Ethoxylates

Shown in Table 1 are the results for the tested ethoxylates. For a given average hydrophobe weight, the presence of branching resulted in modest reductions in pour point and an increase in critical micelle concentration. Interestingly, a Krafft temperature phenomenon was noted in the linear systems which is atypical for nonionic surfactant systems. These systems exhibit decreased solubility both at low temperatures due to crystallinity and at high temperatures where EO dehydration results in phase separation above the cloud point temperature. In contrast, no crystallization occurred at 1% concentration for the branched analogues, i.e., the Krafft temperatures for these systems were below zero. The lower solubility in cold water exhibited by the linear ethoxylates also contributes to the much slower rates of dissolution observed for these systems at 25°C as compared to the respective branched ethoxylates.

Table 1

Physical and Solution Properties of Branch d
and Linear Alcohol Ethoxylates

Surfactant	Pour Point (°C)	Cloud Point (°C)	Krafft Temperature (°C)	Dissolution Time (min.)	Critical Micelle Concentration (ppm)
C14,15-7 (linear)	24	50	25	21	3
2-Alkyl- C14,15-7	14	a)	<0	8	8
C16-9 (linear)	32	63	35	>120	1
RM C16,17-9	21	50	<0	33	4

a) solution was slightly turbid between 0 and 40°C resulting in no distinct cloud point

CONCLUSIONS

The surfactant properties and detergency performance of model 2-alkyl alcohol sulfates have been examined. Addition of a 2-alkyl group reduces the Krafft temperature, improves the calcium tolerance, and the surfactants biodegrade readily.

Additionally:

- laboratory synthesis methods have been developed to prepare random mono-methyl alcohols, which are readily converted to either sulfates or ethoxylates;
- both specific 2-alkyl and random mono-methyl substituents improve the physical chemistry properties of the corresponding alcohol sulfates;
- solubility enhancements are likewise observed for alcohol ethoxylates containing the same branched hydrophobes; and,
- both 2-alkyl branched alcohol sulfates and random mono-methyl sulfates clean well, particularly at cool wash temperatures.

It is expected that a full environmental profile for random methyl substituted surfactants would be favorable: excellent biodegradation is expected, and the combination of good solubility and low sensitivity to water hardness should translate into the ability to wash at lower water temperatures.

REFERENCES

1. Davidsohn, A. S. and B. Milwidsky, "Synthetic Detergents," Seventh Edition, Longman Scientific & Technical, 1987, p. 17.
2. Kravetz, L., J. P. Salanitro, and N. Battersby, "Biodegradation of Alcohol-Based Surfactants Derived from Detergent Range Olefins," presented at the AOCS 85th Annual Meeting & Expo in May, 1994.
3. Götte, E. and M. J. Schwuger, "Überlegungen und Experimente zum Mechanismus des Waschprozesses mit primären Alkylsulfaten" (Theories and Experiments on the Mechanism of Washing with Primary Alcohol Sulfates), translated from *Tenside* 6, 1969, 131-135.
4. March, J., "Advanced Organic Chemistry," John Wiley and Sons, New York, Third Edition, 1985, 411-413.
5. Singleton, D. M., L. Kravetz, and B. D. Murray, US Patent 5,849,960 (Dec. 15, 1998).
6. "Conversion of NEODOL® Alcohols and Ethoxylates to Anionic Surfactants by Sulfation," Shell Chemical Technical Bulletin: 372-80.
7. Reid, V. W., G. F. Longman, and E. Heinerth, "Determination of Anionic-Active Detergents by Two-phase Titration," *Tenside* 4, 1967, 292-304.
8. Raney, K. H., and H. L. Benson, *J. Am Oil Chem. Soc.*, 67, 722 (1990).
9. Raney, K. H., P. G. Shpakoff, and D. K. Passwater, Proc. 4th CESIO World Surfactant Congress, Barcelona, 1996, Vol. 2, p. 50.
10. Rosen, M. J., *Surfactants and Interfacial Phenomena*, John Wiley & Sons, New York, 1978, Chapter 2.
11. Shebs, W. T. and B. E. Gordon, *J. Am. Oil Chem. Soc.*, 45, 377 (1968).
12. Gordon, B. E. and W. T. Shebs, *J. Am. Oil Chem. Soc.*, 46, 537 and references cited therein. See also: Shell Chemical Technical Bulletin: 968:87 (1987) by C. L. Merrill and references cited therein.
13. Sturm, R. N, *J. Am. Oil Chem. Soc.*, 50, 159 (1973).
14. Finger, B. M., G. A. Gillies, G. M. Hartuig, E. R. Ryder, Jr., W. M. Sauyer, and H. Stupel, *J. Am. Oil Chem. Soc.*, 44, 525-530.

A Hachment E



Shell Chemicals

Detergency Performance of the New Selectively Branched Alcohol Sulfates

(at 10°C and 150 ppm Water Hardness)

